

# Dielectric Properties of Teflon from Room Temperature to 314° C and from Frequencies of $10^2$ to $10^5$ c/s<sup>1</sup>

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The dielectric constant and dissipation factor of Teflon were measured at frequencies from  $10^2$  to  $10^5$  c/s and from room temperature to temperatures just below the first-order transition point occurring at 327° C. Measurements of the d-c conductivity were made over the same temperature interval. Results show that the dielectric constant decreases somewhat with increasing temperature. The relation between thermal-expansion coefficient and temperature coefficient of the dielectric constant is roughly as predicted by the Clausius-Mossotti equation. Values of dissipation factor and d-c conductivity at all temperatures are very low (less than  $2 \times 10^{-4}$  and  $2 \times 10^{-15}$  mho/cm, respectively), and the dielectric constant is independent of frequency at all temperatures.

## 1. Introduction

The dielectric behavior of Teflon, an organic high polymer with outstanding temperature stability, is investigated over a wide temperature range with equipment especially designed to permit measurements at elevated temperatures. Previous qualitative investigations [1]<sup>3</sup> have indicated the absence of significant dielectric losses in Teflon up to its first-order transition point at 327° C. No quantitative investigation has been made of the variations of dielectric constant and dielectric loss with temperature. This requires the use of a loss-free micrometer sample holder having the characteristics discussed elsewhere [2].

The following symbols are used in this paper. The subscript 0 refers to room-temperature values.

## 2. Symbols

- $\epsilon'$  = the dielectric constant.
- $\tan \delta$  = the dissipation factor.
- $\epsilon'' = \epsilon' \times \tan \delta$  = the loss factor.
- $f$  = frequency in cycles per second.
- $\omega = 2\pi f$ .
- $\tau$  = relaxation time.
- $C_a$  = the capacitance of a sample of air of the same dimensions as the dielectric measured.
- $D$  = the electrode diameter (2 inches).
- $d$  = the sample diameter
- $s$  = the sample thickness.
- $C$  = the capacitance reading on the internal bridge capacitor with the sample holder connected.
- $C_B$  = the capacitance reading on the internal bridge capacitor with the sample holder disconnected.
- $C_D = C_B - C$  computed at any constant temperature.
- $\Delta C_D$  = the difference between the room temperature value of  $C_D$  and that obtained at another temperature.
- $C_m$  = the computed value of the capacitance of the ring of air located between sample and electrode edges, neglecting edge effects.
- $\Delta C_m$  = the difference between the value of  $C_m$  at any temperature and the room temperature value.

## 3. Methods

### 3.1. Electrical Measurements

The measurements of dielectric constant and dissipation factor were carried out by means of a substitution method, changes in sample capacitance with temperature being followed by balancing with the internal bridge capacitor connected in parallel with the sample holder.

In the experiments to be described, the sample capacitance at room temperature was found by making measurements with the sample between the electrodes and with the sample removed from the electrodes. After the temperature was raised, the sample was kept between the electrodes at all times, and drifts in the bridge were compensated for by disconnecting the sample holder after each reading and by reestablishing the balance with the internal bridge capacitor. The disconnecting was accomplished by means of the special switch built into the sample holder. Details of the measuring equipment are described elsewhere [2].

If it is assumed (1) that the sample expands uniformly in all directions, and (2) that the edge effect at all temperatures is effectively eliminated, we obtain

$$\Delta C_M = \frac{0.08854\pi}{4s_0} [D^2(1-s_0/s) - d_0^2(1-s/s_0)], \quad (1)$$

and the dielectric constant at any temperature is found to be

$$\epsilon' = s_0/s [\epsilon'_0 + (\Delta C_D + \Delta C_m)/C_{a0}]. \quad (2)$$

### 3.2. Sensitivity and Accuracy of Measurements

The sensitivity of the dielectric constant and dissipation-factor measurements was determined by the sensitivity and stability of the bridge elements, as well as by the ratio of sample capacitance to that of the entire arm, consisting of leads, sample holder, sample, and substitution capacitor. It is estimated

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<sup>3</sup>Figures in brackets indicate the literature references at the end of this paper.

that, for the experiments cited, the overall accuracy of the dielectric-constant computations is probably not determined by the accuracy and sensitivity of the dimensional measurements made at room temperature or by the bridge balance, which could be read to  $\pm 0.002 \mu\text{mf}$ . The overall accuracy is determined by deviations from the basic assumptions made, namely, that warping does not take place, that the sample expands uniformly, and that the edge corrections at all temperatures are effectively eliminated. Small deviations from the first two of these assumptions, which are not readily recognizable, are expected to exceed the sensitivity of a room-temperature measurement. It is therefore difficult to make a reliable estimate of the accuracy of the dielectric-constant measurements carried out at higher temperatures. As shown later, the agreement between the several runs was very satisfactory, but an answer to the question of accuracy has to wait for further experiments on samples of widely varying dimensions. The best indication that the dielectric-constant values computed cannot be far from correct is the agreement between the observed and predicted relationship between thermal-expansion coefficient and the temperature coefficient of the dielectric constant. The estimated accuracy of the dissipation-factor measurements is  $\pm 1 \times 10^{-4}$ . The d-c conductivity never exceeded the smallest observable value of  $2 \times 10^{-15}$  mho/cm.

### 3.3. Preparation of Specimens

Molded Teflon undergoes drastic dimensional changes when reheated. It was expected that dimensional stability could be attained by conditioning the samples at a temperature above its  $327^\circ\text{C}$  first-order transition point. Complete stress relaxation and disappearance of all crystallinity at this temperature has been reported [1], and it was therefore expected that the conditioning process would relieve internal strains introduced during molding. This was borne out by the fact that samples that underwent very drastic changes during conditioning for several hours at  $350^\circ\text{C}$  exhibited no further obvious changes when the process was repeated and did not appear to warp during the electrical measurements. Prior to machining, the samples were therefore kept at  $350^\circ\text{C}$  for several hours. They were then machined in a vacuum chuck to give disks approximately  $1\frac{1}{2}$  in. in diameter and approximately  $\frac{1}{8}$  in. thick. As measured by calipers, the faces were flat and parallel to  $\pm 0.0003$  cm and the diameters constant to  $\pm 0.005$  cm, the latter value being determined by the sensitivity of the caliper.

Previous experiments had shown that for accurate measurements over a temperature range it was essential to apply secondary electrodes to the samples. Of the materials tested, evaporated gold was found to be the most satisfactory electrode material, and this was used in all the experiments to be cited.

## 4. Results and Discussion

Measurements were made on samples A and B cut from different sections of a molded rod. Sample B was reannealed as previously described to give sample C. Sample D had been machined from a disk molded separately and came from a different lot than the rod from which the other samples were cut. The values of the dielectric constant at any temperature were not frequency dependent, as will be demonstrated presently, and the values measured at room temperature for samples A, B, C, and D were 2.002, 1.994, 2.016, and 2.022, respectively. The density of the samples was 2.13.

Table 1 gives results for a typical run (sample A) carried out over the entire temperature and frequency ranges. Values of the dielectric constant have been calculated with the aid of eq (1) and (2). It is seen that the values of the dissipation factor, which are of the order of the sensitivity of the bridge, do not show a trend, either with frequency or with temperature. The dissipation factor can, therefore, be represented as having the value of  $(1 \pm 1) \times 10^{-4}$  over the temperature and frequency ranges investigated. Inspection of table 1 also indicates that there is no significant variation of the dielectric constant with frequency at any one temperature. Such a variation would not be expected in view of the very low values of the dissipation factor. The frequency dependence of the dielectric constant can be predicted from the observed values of the loss factor by extending [3] a procedure already described [4] to materials with frequency-independent losses, giving

$$\frac{d\epsilon'}{d \log f} = 2.303 A \epsilon'',$$

where

$$A = \frac{\int_0^{1/\omega} \omega d\tau}{2 \int_0^{1/\omega} \frac{\omega d\tau}{1 + \omega^2 \tau^2}} = 2/\pi,$$

whence

$$\frac{d\epsilon'}{d \log f} = 1.47 \epsilon''.$$

Thus, for Teflon ( $\epsilon' = 2$ ,  $\tan \delta = 1 \times 10^{-4}$ ), a change in dielectric constant of 0.001 over the frequency interval from  $10^2$  to  $10^5$  c/s is computed. This confirms the conclusion, already surmised from table 1, that there is no significant variation of dielectric constant with frequency at any one temperature.

One would expect, therefore, that the variation of dielectric constant with temperature would be caused essentially by the variation in the bulk density of the material. It becomes clear that the accuracy of the dielectric-constant computations depends critically on the validity of the assumptions underlying eq (1)

TABLE 1. Dielectric constant, dissipation factor, and d-c conductivity of Teflon (sample A)

Direct-current conductivity (mho/cm)  $< 2 \times 10^{-15}$  at all temperatures

Temperature	Frequency	Dielectric constant, $\epsilon'$	Dissipation factor, $\tan \delta \times 10^4$
$^{\circ}\text{C}$	c/s		
23	$10^2$	2.001	1
	$10^3$	2.002	-2
	$10^4$	2.003	2
	$10^5$	2.002	0
	$10^6$	1.979	1
86	$10^2$	1.978	1
	$10^3$	1.980	1
	$10^4$	1.979	2
	$10^5$	1.968	1
	$10^6$	1.969	2
113	$10^2$	1.969	1
	$10^3$	1.970	0
	$10^4$	1.958	-1
	$10^5$	1.957	1
	$10^6$	1.959	1
136	$10^2$	1.942	2
	$10^3$	1.944	3
	$10^4$	1.943	1
	$10^5$	1.942	2
	$10^6$	1.902	1
176	$10^2$	1.902	-1
	$10^3$	1.903	2
	$10^4$	1.904	1
	$10^5$	1.876	-1
	$10^6$	1.875	1
219	$10^2$	1.875	2
	$10^3$	1.874	2
	$10^4$	1.813	0
	$10^5$	1.812	1
	$10^6$	1.810	2
276	$10^2$	1.810	2
	$10^3$	1.807	4
	$10^4$		
	$10^5$		
	$10^6$		
314	$10^2$		
	$10^3$		
	$10^4$		
	$10^5$		
	$10^6$		

and on an accurate determination of the sample thickness at all temperatures. Figure 1 shows a plot of relative sample thickness versus temperature. It is seen that the reproducibility is satisfactory and that the experimental values agree with those reported by one of the manufacturers of Teflon. This may be taken as evidence that warping of the sample did not take place to an extent that would seriously influence the results.

Figure 2 is a plot of dielectric constant versus temperature. An average value of the dielectric

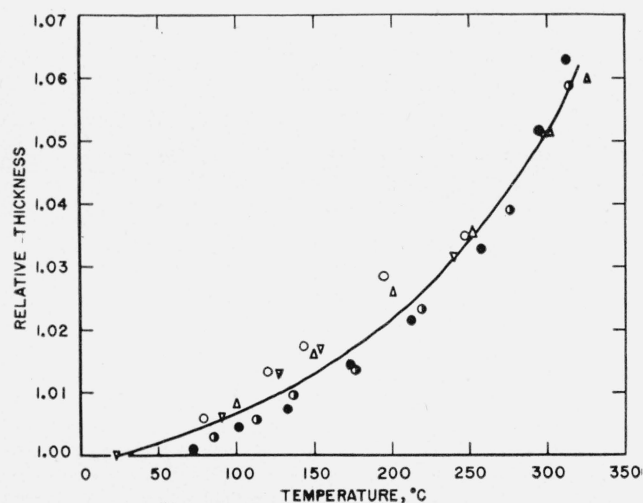


FIGURE 1. Relative thickness of Teflon as a function of temperatures.

●, sample A; ○, sample B; ▽, sample C; ●, sample D; △, expansion measurements made by manufacturer.

constant is used, valid over the entire frequency range and room temperature values of 2.000 have been assumed for each sample in order to obtain a more accurate idea of the reproducibility of the temperature runs. The values used in the plot have therefore been obtained by merely adding or subtracting a small constant correction from the experimental points at all temperatures. As in figure 1, the reproducibility is satisfactory.

The Clausius-Mossotti equation predicts a relation between the temperature coefficient of the static dielectric constant and the linear thermal-expansion coefficient,  $\alpha_l$ , which, in the case of a nonpolar material like Teflon, one might expect to be applicable to the dielectric constant at audio and radio frequencies. Similar relations can be derived for other theories, but we shall assume the validity of the Lorentz field and therefore of the Clausius-Mossotti equation, obtaining [5]

$$\frac{d\epsilon'}{dT} = -\alpha_l(\epsilon' - 1)(\epsilon' + 2).$$

In the case of Teflon, the value of  $-(d\epsilon'/dT)/\alpha_l$  predicted on the basis of the above equation would therefore range from roughly 3.85 at 100° C. to roughly 3.5 at 250° C. The experimental values range from 3.6 at 100° C to 3.0 at 250° C.

In view of the assumptions underlying the evaluation of the experimental dielectric constants, this comparison would seem at least not to be in disagreement with the Clausius-Mossotti theory, although a truly quantitative test on this basis would seem to be impossible.

The sensitivity of the bridge is much too low to obtain even a qualitative idea of the behavior of the dielectric losses as a function of temperature and frequency. Table 1 indicates that the values of the

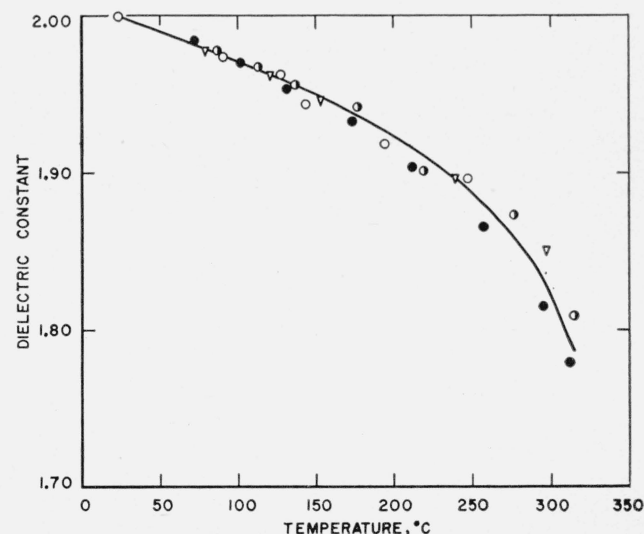


FIGURE 2. Dielectric constant of Teflon at any frequency between  $10^2$  and  $10^5$  c/s as a function of temperature.

●, sample A; ○, sample B; ▽, sample C; ●, sample D.

dissipation factor are of the order of  $10^{-4}$ . No satisfactory data on nonpolar polymers with losses of that order of magnitude have as yet been published, and theories [6, 7] put forward to explain the nature of such losses have therefore remained untested.

Quantitative information on phase transitions in Teflon is available both on the basis of dilatometric [8] and of thermodynamic measurements [9]. These investigations agree as to the occurrence in the room-temperature range of a double first-order transition, both steps of which presumably occur between crystalline forms, the less pronounced step occurring at about 30° C, whereas the one involving the larger volume change occurs at about 20° C. The volume changes associated with this transition were not indicated by the thickness measurements made on the sample in the holder because these measurements were very crude compared to dilatometric measurements. The fact that there appears to be no drastic change in dielectric constant in this region does not appear surprising if one assumes that the transition occurs between essentially nonpolar crystals. The high-temperature melting transition at 327° C can be easily indicated by the dielectric measurements as it is associated with dimensional changes of sufficient magnitude to result in large capacitance changes. There was considerable warping of the sample at this temperature, and attempts to carry out reproducible measurements through this transition range were abandoned.

## 5. Summary

The variation of the dielectric properties of Teflon from 24° to 314° C can be accounted for in terms of the variation of the bulk density of a nonpolar material.

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## 6. References

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